WITH EACH NEW GENERATION OF MATERIALS SYNTHESIZED COMES A NEW SET OF CHALLENGES TO UNDERSTAND AND EXPLOIT
OUTLINE

➤ Correlation

➤ Why is the problem of electronic structure hard?

➤ Mean field approaches (independent-particle picture):
   1. Hartree-Fock method
   2. Kohn-Sham approach

➤ What is meant by electron correlation?

➤ Weak vs strong correlation
CORRELATION IN EVERYDAY LIFE

In a many body system, the behaviour of a given entity is not independent of the others!
CORRELATION IN MATHEMATICS & NATURAL SCIENCES

\[ \langle AB \rangle \neq \langle A \rangle \langle B \rangle \]

\[ C_{AB} = \langle AB \rangle - \langle A \rangle \langle B \rangle \]

➤ Spatial

\[ \langle n(r, t)n(r', t) \rangle \neq \langle n(r, t) \rangle \langle n(r', t) \rangle \]

➤ Temporal

\[ \langle n(r, t)n(r, t') \rangle \neq \langle n(r, t) \rangle \langle n(r, t') \rangle \]
ELECTRON CORRELATION
PECULIARITY
QUANTUM MECHANICS,
INDISTINGUISHABLE PARTICLES
MANY-BODY PROBLEM IN SOLIDS

➤ Many-body Hamiltonian of an electronic system

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \hat{\nabla}_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{e^2}{|\hat{r}_i - \hat{r}_{i'}|} - \sum_{i \hat{\alpha}} \frac{Z_\alpha e^2}{|\hat{r}_i - \hat{R}_\alpha|} \]

\[ - \sum_{\alpha} \frac{\hbar^2}{2M_\alpha} \hat{\nabla}_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z'_\alpha e^2}{|\hat{R}_\alpha - \hat{R}_{\alpha'}|} \]

➤ Many-body wave-function for N electrons

\[ \Psi(\mathbf{r}_1 \sigma_1, \ldots, \mathbf{r}_N \sigma_N) \]
Trial many-body wave function for an N electrons system

\[ \Psi(r_{1\sigma_1}, \ldots, r_{N\sigma_N}) = \sum_i c_i \psi_i(r_{1\sigma_1}, \ldots, r_{N\sigma_N}) \]

\[ \langle \Psi | \hat{H} | \Psi \rangle = \sum_{ij} c_i^* c_j \langle \psi_i | \hat{H} | \psi_j \rangle \]

Many-body basis set?

Product of one-particle wave-functions

Choose M (M>N) single particle basis function (spin-orbital)

\[ \{ \phi_{1\sigma_1}(r), \phi_{2\sigma_2}(r), \ldots, \phi_{M\sigma_M}(r) \} \]

Electrons are indistinguishable fermions

\[ \Psi(r_{1\sigma_1}, r_{2\sigma_2}) = -\Psi(r_{2\sigma_2}, r_{1\sigma_1}) \]
HYDROGEN MOLECULE

➤ A two electrons example

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_{\alpha=1}^{2} \frac{Z_\alpha e^2}{|\hat{r} - \mathbf{R}_\alpha|}
\]

➤ Basis set for singlet configuration

\[
\begin{align*}
\psi_4 &= \frac{1}{\sqrt{2}} \left[ \phi_u(1)\chi^\uparrow(1)\phi_u(2)\chi^\downarrow(2) - \phi_u(1)\chi^\downarrow(1)\phi_u(2)\chi^\uparrow(2) \right] \\
\psi_3 &= \frac{1}{\sqrt{2}} \left[ \phi_g(1)\chi^\uparrow(1)\phi_u(2)\chi^\downarrow(2) - \phi_u(1)\chi^\downarrow(1)\phi_g(2)\chi^\uparrow(2) \right] \\
\psi_2 &= \frac{1}{\sqrt{2}} \left[ \phi_u(1)\chi^\uparrow(1)\phi_g(2)\chi^\downarrow(2) - \phi_g(1)\chi^\downarrow(1)\phi_u(2)\chi^\uparrow(2) \right] \\
\psi_1 &= \frac{1}{\sqrt{2}} \left[ \phi_g(1)\chi^\uparrow(1)\phi_g(2)\chi^\downarrow(2) - \phi_g(1)\chi^\downarrow(1)\phi_g(2)\chi^\uparrow(2) \right]
\end{align*}
\]

\[
\Psi \simeq c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + c_4 \psi_4
\]
WHY IS THE PROBLEM OF ELECTRONIC STRUCTURE HARD?

- N electrons system and M (M>N) single particle basis function
  \[ \Psi(r_1\sigma_1, \ldots, r_N\sigma_N) = \sum_i c_i \psi_i(r_1\sigma_1, \ldots, r_N\sigma_N) \]

- Number of Slater determinants
  \[ \binom{M}{N} = \frac{M!}{N!(M-N)!} \]

- Two carbon atoms (N=12). Suppose M=36
  more than \(10^9\) determinants

Dimensionality
IT IS HOPELESS TO LOOK FOR AN EXACT SOLUTION OF A MANY-BODY SYSTEM

How we are going to proceed?
MEAN FIELD APPROACHES

spatial and temporal correlation

structureless cloud: particles are uncorrelated except that they obey the exclusion principle

Fig. from K. Held

Coulomb interaction
⇒ correlations

Fig. from G. Kotilar et al

time-averaged electron density

lattice potential

Fig. from ChemTube3D
HARTREE-FOCK METHOD

- A wave function composed of a single Slater determinant

\[ \psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1 \sigma_1) & \phi_2(r_1 \sigma_1) & \cdots & \phi_N(r_1 \sigma_1) \\ \phi_1(r_2 \sigma_2) & \phi_2(r_2 \sigma_2) & \cdots & \phi_N(r_2 \sigma_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_N \sigma_N) & \phi_2(r_N \sigma_N) & \cdots & \phi_N(r_N \sigma_N) \end{vmatrix} \]

- The single-electron functions are chosen cleverly to produce the best approximation possible

\[ \delta \langle \psi | H | \psi \rangle / \delta \phi_i^* = 0 \]

\[
- \left( \frac{\hbar^2}{2m_e} \nabla^2 + \sum_{\alpha} \frac{Z_\alpha e^2}{|r - R_\alpha|} \right) \phi_i(r) + \sum_{j}^{\text{occ}} \int dr' \phi_j^*(r') \frac{e^2}{|r - r'|} \phi_j(r') \phi_i(r) - \sum_{j}^{\text{occ}} \int dr' \phi_j^*(r') \frac{e^2}{|r - r'|} \phi_i(r') \phi_j(r) = \epsilon_i \phi_i(r)
\]
SLATER DETERMINANTS ARE UNCORRELATED

- The repulsion energy between two electrons is calculated between an electron and the average electron density for the other electrons.

It doesn't take into account the fact that the electron will push away the other electrons as it moves around.

- Probability density of finding two electrons

\[ \rho(r_{1\sigma_1}, r_{2\sigma_2}) = \sum_{\sigma_3...\sigma_N} \int dr_3 \ldots dr_N |\psi(r_{1\sigma_1}, \ldots, r_{N\sigma_N})|^2 \]

\[ = \frac{1}{N(N-1)} \sum_{kl} [|\phi_k(r_{1\sigma_1})|^2 |\phi_l(r_{2\sigma_2})|^2 - \phi^*_k(r_{1\sigma_1})\phi_k(r_{2\sigma_2})\phi^*_l(r_{2\sigma_2})\phi_l(r_{1\sigma_1})] \]

\[ \rho(r_1, r_2) = \sum_{\sigma_1\sigma_2} \rho(r_{1\sigma_1}, r_{2\sigma_2}) \]

Opposite spin orbitals are uncorrelated!
Kohn–Sham Approach

- It is not essential to tabulate the complete many-body wave function.

- The Kohn-Sham approach to DFT defines an auxiliary system of independent fermions that is chosen to reproduce the ground state electron density but not all properties.

- DFT guarantees us that such an auxiliary system exist end even more provides us a generator for its external potential:

\[
\left( -\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{eff}}(r) \right) \phi_i(r) = \epsilon_i \phi_i(r)
\]

\[
n(r) = \sum_i f_i |\phi_i(r)|^2
\]

\[
v_{\text{eff}}(r) = v_{\text{ext}}(r) + v_H([n], r) + v_{xc}([n], r)
\]

Universal exchange-correlation functional.
WHAT IS MEANT BY ELECTRON CORRELATION?

➤ Chemist: what is not captured in Hartree-Fock method

➤ Correlation energy

\[ E_{\text{corr}} = \langle \Psi | H | \Psi \rangle - E_{\text{HF}} \]

\[ |\Sigma(\omega) - \Sigma_{HF}| \]

➤ Physicist: what is not captured in Khon-Sham approach in LDA/GGA approximation

➤ Correlation energy

\[ E_{\text{corr}} = \langle \Psi | H | \Psi \rangle - E_{\text{LDA/GGA}} \]

\[ |\Sigma(\omega) - \nu_{xc}^{\text{LDA/GGA}}| \]
A weakly-correlated system is one for which a mean-field approximation or a low-order perturbation expansion around it suffices.
ELECTRON CORRELATION SIGNATURES

Thermodynamic and transport properties which are fundamentally different from mean-field theory or Landau Fermi-liquid theory predictions
OUTLINE

➤ Adiabaticity
➤ Landau Fermi liquid
➤ Quasi-particles vs original electrons
➤ When is the independent-particle picture not sufficient?
➤ Electron correlation signatures
➤ Beyond mean field approaches
  1. Dynamical mean field theory
  2. Quantum Monte Carlo
➤ Correlation induced metal-insulator transition
Labels associated with eigenstates are more robust against perturbations than the eigenstates themselves.

\[
\frac{-1}{2} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi
\]

\[V(x) = \begin{cases} 
\frac{1}{2} \lambda x^2 & |x| < \pi, \\
\infty & |x| \geq \pi.
\end{cases}\]

Fig. from A. J. Schofield
ADIABATIC EVOLUTION

\[ H(t) = H_0 + \lambda(t)(H - H_0) \]

\[ \lambda(t) = e^{-|t|\delta} \]

Fig. from P. Coleman
LANDAU FERMI LIQUID

- Landau argued that the ground state of a non-interacting system (Fermi sea) adiabatically evolves into the ground state of the interacting system

- Conserved quantum numbers: spin, charge and momentum
QUASI-PARTICLES

➤ Each quasiparticle contributes additively to the total entropy of the system but not to the energy

➤ A quasiparticle’s energy also depends on the distribution of other quasiparticles

➤ The inertial mass of the quasiparticle is modified by the backflow \( m \rightarrow m^* \)

\[
m^* = m(1 + F_1^s)
\]

\[
v_F = \frac{P_F}{m^*} = \frac{P_F}{m} - \frac{P_F}{m} \left( \frac{F_1^s}{1 + F_1^s} \right)
\]

Fig. from P. Coleman
Quasi-particle lifetime

- Quasiparticles and holes are only approximate eigenstates of the system.
- Decay rate of a quasiparticle with energy $\varepsilon$ above the Fermi surface at $T=0$ is
  \[ \frac{1}{\tau_\varepsilon} \propto \varepsilon^2 \]
- Quasiparticle is well defined close to the Fermi level.
- At $T>0$, the scattering rate goes like $T^2$.
WHAT ABOUT ELECTRON THEMSELVES?

➤ There must remain a fraction of the original non-interacting excited state wave function in the quasiparticle wave function

\[ \tilde{\phi}_{QP}(k\sigma) = \sqrt{z}\phi_{el}(k\sigma) + \text{particle} - \text{hole excitations etc.} \]

➤ The fraction, \( z < 1 \), plays the role of the order parameter of the zero temperature Fermi liquid state.
PHOTOEMISSION SPECTROSCOPY

➤ Spectral function: A tool for following the fate of the original electrons
<table>
<thead>
<tr>
<th></th>
<th>Low T, (T\ll T_D)</th>
<th>High T, (T\ll T_D)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Debye temperature: T_D</td>
<td></td>
</tr>
<tr>
<td>Resistivity</td>
<td>$A_{\text{imp}} + B_{\text{e-e}}T^2 + C_{\text{e-ph}}T^{d+2}$</td>
<td>$C'_{\text{e-ph}}T$</td>
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<tr>
<td>Seebeck coefficient</td>
<td>$DT + E_{\text{phd}}T^d$</td>
<td>$D'<em>{\text{e-ph}}T + E'</em>{\text{phd}}T^{-1}$</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>$H_{\text{e-e}}T^{-1} + L_{\text{imp}}T + G_{\text{e-ph}}T^{d-1}$</td>
<td>$G'_{\text{e-ph}}$</td>
</tr>
<tr>
<td>Specific heat</td>
<td>$\gamma T$</td>
<td></td>
</tr>
</tbody>
</table>
WHEN IS THE INDEPENDENT-PARTICLE PICTURE NOT SUFFICIENT?

➤ Electrons hesitate between being localized on short time scales and itinerant on long time scales

➤ Some phase transitions and ordered states: ordered magnetic states

➤ Screening

➤ Strange metals (Non-Fermi liquid behaviour)

➤ Strong fluctuations between different low-energy fermionic configurations
SIGNATURES OF ELECTRON CORRELATION

- Correlation-induced phase transition
- Differences between LDA band masses and measured masses
- Satellites in photoemission
- Non-linear T dependance of the electronic contribution in specific heat
- Small Drude weights

Fig. from P. D. C. King et al LaNiO$_3$ film

CeNiAs$_{1-x}$P$_x$O (Fig. from Y. Luo et al)
BEYOND MEAN-FIELD APPROACHES

➤ Dynamical mean-field theory
CORRELATION DRIVEN METAL-INSULATOR TRANSITION

➤ VO$_2$
SUMMARY

➤ Most materials with interesting properties such as heavy fermion, high $T_c$ superconductor, giant magnetoresistance, multiferroic etc. are strongly correlated

➤ Ordered states are usually weakly correlated

➤ Methods such as QMC (model Hamiltonian) or LDA+DMFT take into account some correlation effects